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(54) Determining the wax appearance point and wax content of petroleum products.

(57) Concerns a method for determination of wax appearance point and quantity of wax in petroleum products and the equipment required for this. The wax appearance point is determined by measuring the change in volume as a function of temperature as the appearance point appears as a deviation in this graph. The quantity of wax which appears is determined by comparing the measured volume graph as a function of temperature with the estimated volume graph. The equipment which is used comprises a pressure cell (2) located in a thermostat bath (1), to which is connected a control unit (7) for reading off and setting the pressure (4), temperature (5) and volume (6).

Fig. 1

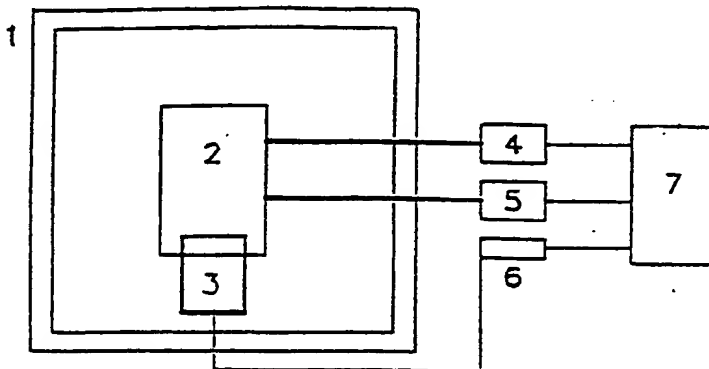


Fig. 1

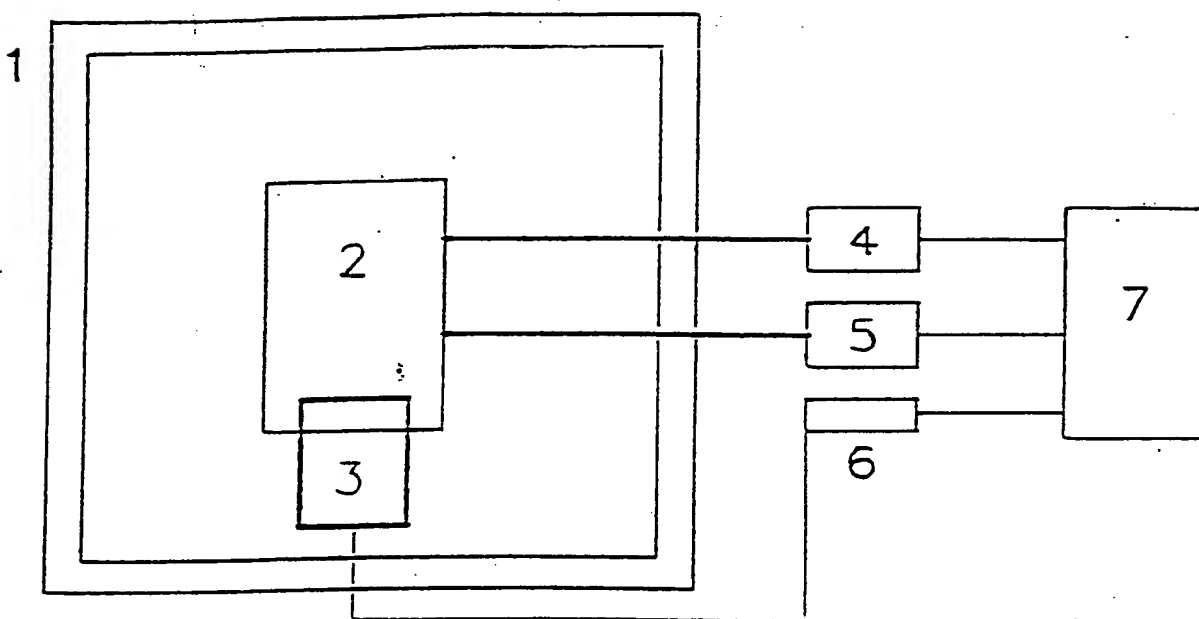


Fig. 2

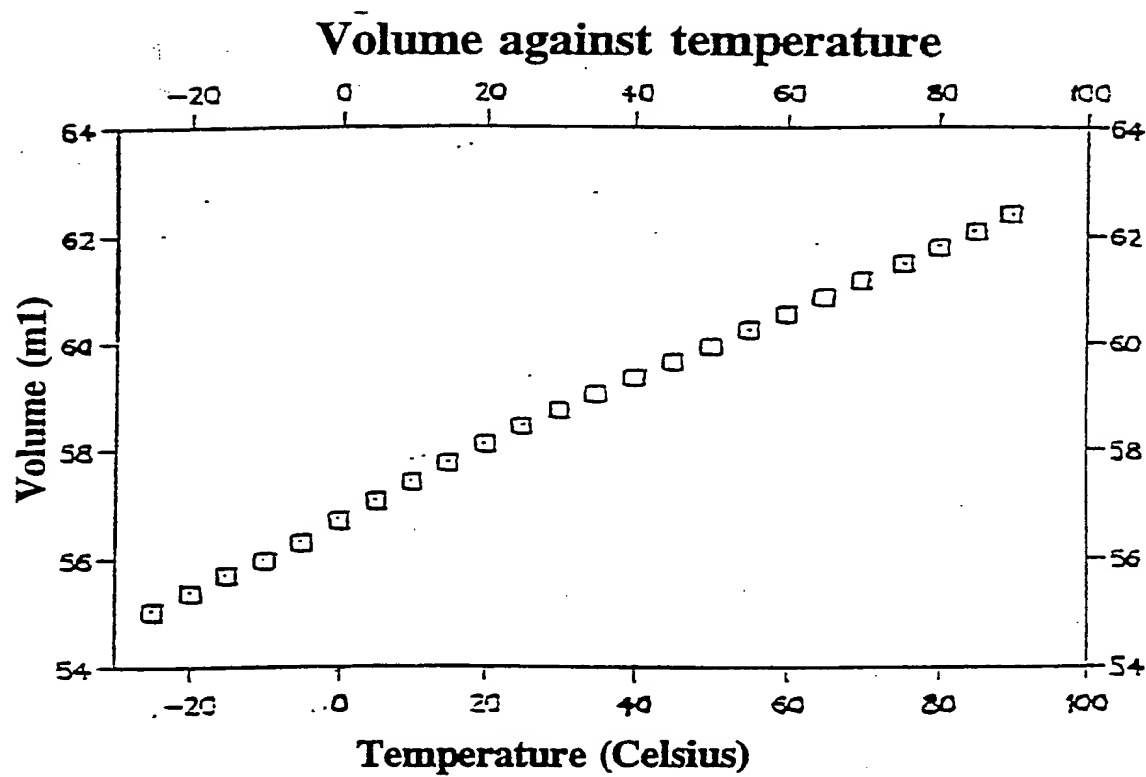


Fig. 3

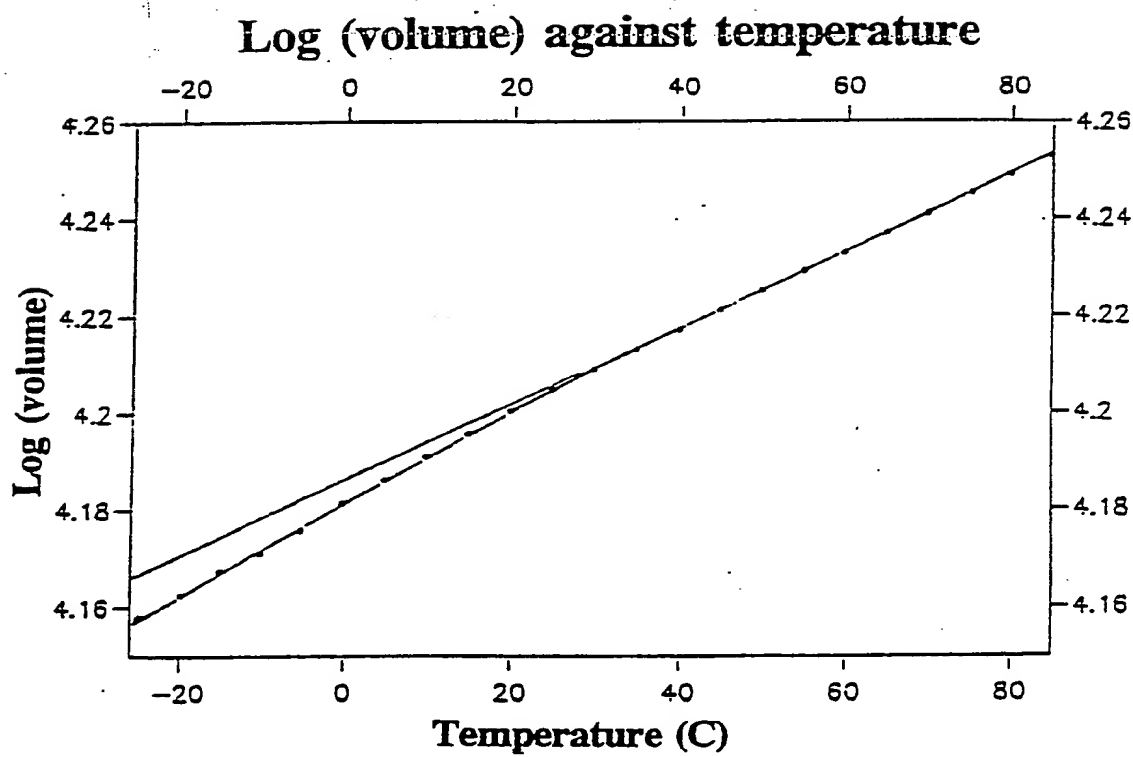
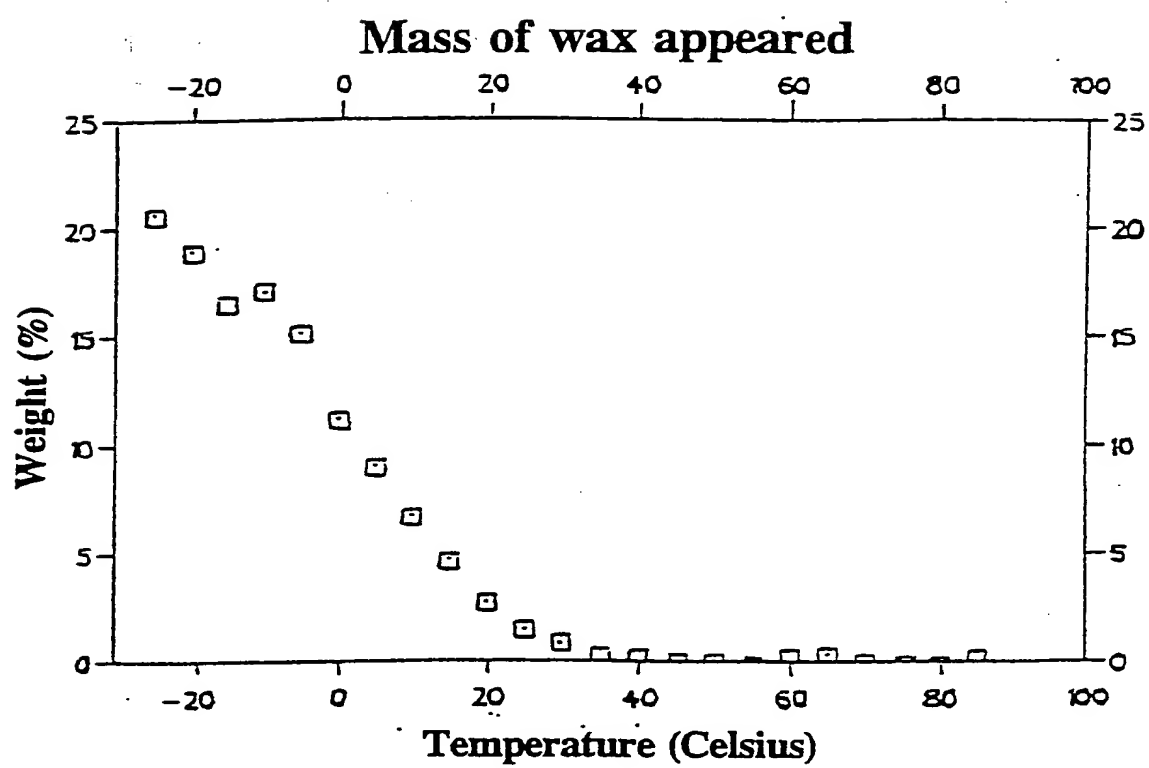


Fig. 4



The present invention relates to methods and apparatus for determining the wax appearance point and the quantity of wax in petroleum products.

Oil, or hydrocarbon fluid, has a complex composition and the number of individual components is so large as to be difficult to estimate in practice. A distinction is made between straight-chained paraffins (n-paraffins), branched paraffins (isoparaffins), naphthenes (cycloparaffins) and aromatic compounds. In addition, there are smaller quantities of compounds such as asphaltenes and resins. These are compounds which contain heteroatoms (oxygen, nitrogen and sulphur) as well as heavy metals. It is also important to distinguish between stabilized oil (without gas) and real fluid (with gas, such as occurs in a reservoir). The content of light hydrocarbons (C_1 to C_6) in real fluid is in the order of 20 mol% higher than for stabilized oil.

For the straight-chained paraffins, the change in physical properties is proportional with the increase in chain length. The branched paraffins have less predictable properties. An increasing level of branching will, in most cases, lead to a reduction in the boiling point and melting point. The content of the various paraffin isomers in a "normal" North Sea oil will be distributed in such a way that there is a majority of straight-chained paraffins and only small quantities of each individual isomer. The reasons for this are to be found in the geological origin of the oil, the conditions in the types of source rocks and the reservoir, as well as the large number of possible isomers with the same carbon chain length.

For wax appearance this means that it is very difficult to characterize the appeared material. The wax which appears will mainly be normal paraffins on account of the higher content of these components and because the melting points for n-paraffins are considerably higher than for most other components in the oil. Models which are based on a wax fraction which is dissolved in the rest of the oil must therefore have a good analytical description of the composition of the complete fluid, in both its solid and liquid phase. With the analytical techniques which exist today this is not a realistic proposition.

The content of light components in the fluid influences the solubility of the more long-chained components at a given temperature. In addition, the increase in pressure, as a function of the increased content of light components, will have an effect on the properties of the components in the oil and therefore also on the solubility. The net effect of the increased pressure and the increased content of light components will therefore be dependent on the total composition of the fluid.

Traditional methods for determining wax content in oil are "wax appearance point", i.e. the temperature at which wax appears in a petroleum product, by means of polarisation microscopy, "pour point" and UOP wax content.

Microscopy. A drop of oil (heated to 80°C) is placed between two object-glasses. The oil is observed through a microscope (125x magnification). Polarized light is passed through the film of oil and further through a polarization filter which extinguishes all light. If crystals have formed in the oil the polarized light is deflected and is not extinguished by the filter. This is observed through the microscope as luminous spots, corresponding to wax crystals. The method is dependent on the thickness of the wax film, the cooling speed (supercooling, equilibrium) and it is operator-dependent. Furthermore it is probable to assume that the composition of the oil will influence the level of supercooling and the equilibrium time for the formation of wax crystals. It is

also generally preferable to use a system which measures the wax appearance point, WAP, by means of equilibrium and not by cooling at a given rate as this method involves. This method can only be used in stabilized oils.

Pour point. This method is carried out in accordance with ASTM D97-66 (1980 part 23). The pour point is defined as the temperature at which there is no movement in the sample when the sample bottle is held horizontally for 5 seconds. The sample is cooled from 80 degrees at a rate of 12 degrees/hour and the pour point is checked every 2°C. The method gives a figure for the flow properties of the stabilised oil.

UOP wax content. This method is described by Burger, E.D. et. al, J. Pet. Tech., 1981 (June), 1075-1086. The method is based on determining the components of the oil which are insoluble in acetone at -18°C. This is a definition of wax which is difficult to relate to the real wax content. Furthermore, it cannot be used for real fluid.

When designing development solutions for marginal oil fields (sub-sea solutions etc.) it can be of decisive importance whether the effect of light components and increased pressure is positive or negative on the wax appearance point, the pour point and the quantity of wax as a function of temperature. This is because of the costs associated with the inhibition of wax, pigging facilities in the pipeline systems, insulation and any injection of solvents and hot oil. Furthermore, it will be of interest to know the temperature for gelling in connection with blocking the pipeline and any problems with starting up after such gelling. Wax deposits can also lead to problems in connection with inspection of pipelines for corrosion etc.

Today there is no accepted method for determining the wax appearance point and the quantity of wax in real fluid.

On the basis of this it was therefore desirable to develop a method for determining the wax appearance point and the quantity of wax under real pressure and gas

saturation.

In a first aspect, a method of determining the wax appearance point in petroleum products in accordance with the invention comprises measuring and plotting graphically the volume of the petroleum product as a function of temperature at constant pressure, wherein the wax appearance point occurs at the temperature at which there is a deviation in the graph.

In accordance with a second aspect of this invention, a method of determining the quantity of wax in a petroleum product at a particular temperature comprises estimating the density of the solid and liquid wax, measuring the change in volume of the petroleum product due to the phase transition between a temperature at which all the wax is in solution in the petroleum product and the said particular temperature and multiplying the estimated density by the measured volume change.

The procedure which constitutes the present invention is based on phase changes in the fluid in connection with a change in temperature. This has the advantage that a change in the properties of the fluid is measured which can be directly explained by the transition from liquid to solid phase.

The methods in accordance with the present invention can be used on fluids with the degree of saturation and pressure which are relevant in the various field solutions. The effect of the changes in the fluid in connection with, for example, addition of an inhibitor or mixture of different fluids in the transportation pipelines etc. can easily be studied.

Apparatus in accordance with this invention for determining the volume of petroleum products comprises a pressure cell arranged in a thermostat bath, a pump connected to the pressure cell for producing pressure, sensors for measuring pressure, temperature and volume in the cell and a control unit for reading and setting the pressure, temperature and volume of the cell.

The present invention will now be described by way

of examples, and with reference to the accompanying drawings, in which:

Fig. 1 shows a schematic representation of an apparatus for determining the volume of petroleum products in accordance with the present invention.

Fig. 2 shows graphically the measured volume of an oil as a function of temperature.

Fig. 3 shows graphically the logarithm of the volume as a function of temperature using data from Fig. 2 and

Fig. 4 shows a diagram for determining the quantity of wax which appears, using data from Fig. 2.

The equipment is visually represented in Fig. 1, in which the symbols 1-7 stand for:

1. Thermostat bath, air.
2. Pressure cell with sample.
3. Pump with motor to regulate the pressure.
4. Pressure sensor.
5. Temperature sensor.
6. Volume reading.
7. Control unit for reading and setting the pressure, temperature and volume.

If the oil cools without the appearance of solid phases the oil will follow a normal exponential volume dependence on temperature. If the temperature interval is not too large it can be assumed that the thermal expansivity, α , is constant and defined as usual:

$$\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = \alpha \quad 1$$

where V is the volume of the sample, T the temperature and p the constant pressure by derivation. This can be integrated in the usual way to produce the following equation:

$$V = V_0 e^{\alpha(T-T_0)} \quad 2$$

The integration takes place from T_0 to T which gives the volumes V and V_0 .

By transferring an oil sample to a volumetrically calibrated pressure cell, setting the pressure to a given value and taking readings at equilibrium, the volume V can be followed as a function of the temperature T .

The appearance of a solid phase will cause the above equations no longer to apply for the whole system (solid + liquid). The system is then heterogeneous and the individual phases are best treated individually.

Solid crystalline phases usually have a greater density than the corresponding liquid phases. Therefore with phase transitions of pure components a jump in volume occurs, measured against temperature. As described, oil is a mixture of many components and the conditions are therefore more complex. When the freezing point of some of the wax is reached, these components will precipitate. This causes a change in density which can, in turn, be observed as a change in volume beyond that described in the equations above.

In other words, from the wax appearance point down the change in volume will be due to two elements: 1) expansivity to the liquid phase and 2) the difference in volume between the solid and liquid wax.

Measurements show that appearances of wax can be detected by measuring the volume as a function of temperature at constant pressure. The change in volume can be divided into two elements, as described above. The size of the element from the phase transition is dependent on the quantity of wax which appears per degree. Fig. 2 shows a measured volume graph for an oil. As can be seen, the volume change due to the phase transition is low but detectable.

All measurements were taken in an optical cell 2 as shown in Fig. 1, i.e. the whole sample volume was visible. The visually observed wax appearance point complied to a high degree with the volume observations. This crude oil was transparent with both laser light and normal light. The wax appearance could be observed as a strong increase in the

dispersion of the light from the laser beam and the precipitation was visible in normal light.

The wax appearance is thus determined by means of two independent methods and the results are in accordance with one another.

The simplest method for determining the appearance point is to linearise equation 2. Taking logarithms on both sides of the equation produces a straight line:

$$\ln V = \ln V_0 + \alpha(T - T_0)$$

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The measured quantities are V and T . A graph is plotted of $\ln V$ against T . If the oil does not contain appeared wax, the points will lie in a straight line. With wax appearance it will be possible to observe significant and systematic deviations from this line. This technique does not require that V_0 and T_0 be determined. Equation 3 can also be written:

$$\ln V = \ln V_0 - \alpha T_0 + \alpha T = \text{Const.} + \alpha T$$

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where V_0 and T_0 are combined in the constant. Fig. 3 shows the result of this procedure on data from Fig. 2. It can be seen that the appearance point is easier to observe in Fig. 3 than in Fig. 2.

By estimating the density of the solid and liquid wax and measuring the change in volume due to the phase transition, the quantity of wax which has appeared can be determined. Fig. 4 shows a result of this procedure. The density of the liquid wax in the mixture is difficult to estimate. The results must therefore be used with some caution.

CLAIMS

1. A method of determining the wax appearance point in petroleum products, comprising measuring and plotting graphically the volume of the petroleum product as a function of temperature at constant pressure, wherein the wax appearance point occurs at the temperature at which there is a deviation in the graph.

2. A method as claimed in Claim 1, comprising plotting graphically the volume of the petroleum product on a logarithmic scale as a function of temperature, wherein the wax appearance point occurs at the temperature at which there is a deviation in the graph.

3. A method as claimed in Claim 2 wherein the deviation in the graph appears by following the function for expansivity, when $\alpha = [\ln(V/V_0)] / T$, where V_0 is the volume of the petroleum product at $T = T_0$ which is set at 0°C given that no wax has appeared at that temperature.

4. A method of determining the quantity of wax in a petroleum product at a particular temperature comprising estimating the density of the solid and liquid wax, measuring the change in volume of the petroleum product due to the phase transition between a temperature at which all the wax is in solution in the petroleum product and the said particular temperature and multiplying the estimated density by the measured volume change.

5. A method as claimed in Claim 4 wherein the volume is measured as a function of temperature at constant pressure.

6. Apparatus for measuring the volume of petroleum products, comprising a pressure cell arranged in a thermostat bath, a pump connected to the pressure cell for producing pressure, sensors for measuring pressure,

temperature and volume in the cell and a control unit for reading and setting the pressure, temperature and volume of the cell.

7. Apparatus as claimed in Claim 6 wherein the pump is a piston pump.

8. Apparatus as claimed in Claim 7 wherein the change in volume in the cell is measured by means of a sensor which registers the position of the piston in the piston pump.

9. Apparatus substantially as hereinbefore described and with reference to Figure 1 of the accompanying drawings.

Patents Act 1977
Examiner's report to the Comptroller under
Section 17 (The Search Report)

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Relevant Technical fields

- (i) UK Cl (Edition L) G1S - SQA
G1D - DHX
- (ii) Int Cl (Edition 5) G01N - 25/02, 25/12, 33/26,
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Search Examiner

B F BAXTER

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25 AUGUST 1993

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASE: WPI

Documents considered relevant following a search in respect of claims 1-3

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
	NONE	

Category	Identification of document and relevant passages - -	Relevant to claim(s)

Categories of documents

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